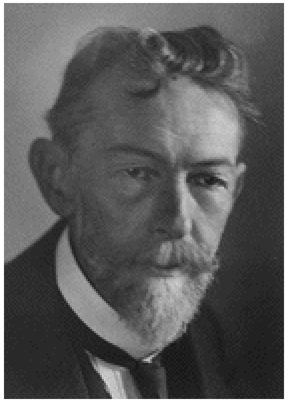
Colloids



Richard Adolf Zsigmondy
Chemistry Nobel, 1925

"Around the middle of the 19th century the English scientist Graham put forward a new principle of subdividing matter by classifying all substances into one of the two great classes: crystalloids and colloids. A crystalloid, e.g. common salt, is characterized in that it passes in the dissolved state readily through membranes such as parchment paper or collodion films and also that it exhibits a rapid free diffusion. A colloid, on the other hand, e.g. glue, is unable to pass through such membranes and diffuses extremely slowly, in contrast to the crystalloid. In passing it may be mentioned that the name colloid originates precisely from *kolla*, the Greek word for glue. Other examples of colloids well known to everyone are proteins, starch, rubber, water glass, *etc*."

From nobel.se

Colloids

The forces of nature:

1. Strong forces hold protons and neutrons together (exchange of mesons)
2. Weak interactions are involved in some kinds of radioactive decay (β-decay)
3. *Coulombic or electrostatic forces hold most matter together*
4. Gravitation forces affect tides, hold us to the earth *etc.*

Israelachvili, Intermolecular and Surface Forces

Complete and precise descriptions based on quantum mechanics exist for the Coulombic/Electrostatic force. These are used to describe materials.

Interactions in colloids are usually described in simple terms.

Colloids

Gravity and the forms of potentials:

$$F = -\frac{\partial U(r)}{\partial r} = \frac{Gm_1m_2}{r^2}$$

Gave rise to the historical belief that the forces between atoms, molecules *etc.* could be expressed in a form that related force (or the potential) to the interatomic/intermolecular distance.

The first serious attempts arose from the van der Waals equation of state:

$$(P + a/V_m^2)(V_m - b) = RT$$

If $a = b = 0$, then one recovers the ideal gas. a represents the effect of attraction between molecules and b, their volume. Mie in 1903 proposed the general form of an intermolecular potential:

$$U(r) = -A/r^n + B/r^m$$

Colloids

Limits on a potential of the form: $U(r) = A/r^n$

In a homogeneous medium, the total energy from a central molecule to all molecules as one moves to some maximum length is given by the integral from the molecular radius to the maximum length:

$$\int_\sigma^L U(r)4\pi\rho r^2\mathrm{d}r = -4\pi A\rho \int_\sigma^L r^{2-n}\mathrm{d}r$$

$$= -\frac{4\pi A\rho}{(n-3)\sigma^{n-3}}\left[1-\left(\frac{\sigma}{L}\right)^{n-3}\right]$$

$$= -\frac{4\pi A\rho}{(n-3)\sigma^{n-3}} \quad \text{for} \quad n>3 \quad \text{and} \quad L>>\sigma$$

Note that $n>3$ is a necessary condition for the more distant molecules to not dominate in the potential. What about gravity and luminous intensity from the stars ?

Israelachvili, Intermolecular and Surface Forces

Colloids

The hard sphere potential:

$$U(r) = 0 \text{ for } r \geq \sigma \text{ and } U(r) = \infty \text{ for } r < \sigma$$

This is sufficient to crystallize materials (the Alder transition):

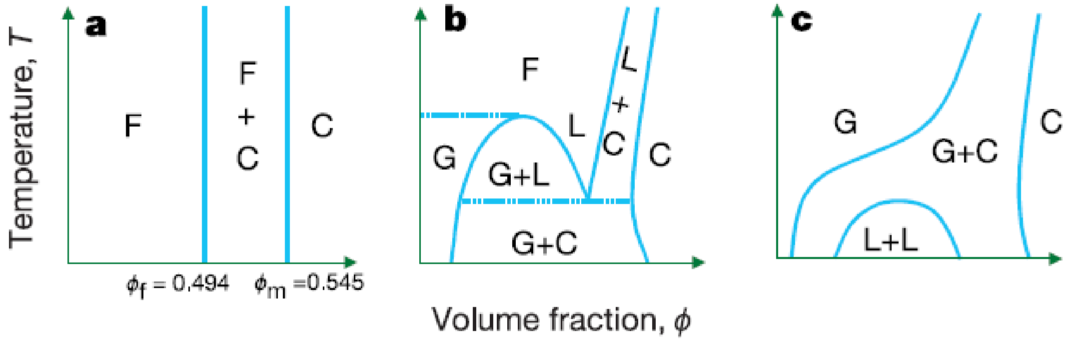


Figure 1 A wide range of phase diagrams occurs naturally. **a**, For a purely hard-sphere system the phase diagram shows only fluid (F) and crystal (C) phases. **b**, Atomic systems are often modelled by hard spheres with long-range attractions. This leads to equilibrium between gas (G), liquid (L) and crystal phases. **c**, In cases where the attraction is short-range, as in protein systems (important in physiology), equilibrium between gas and crystal is found, but the liquid–liquid transition becomes metastable.

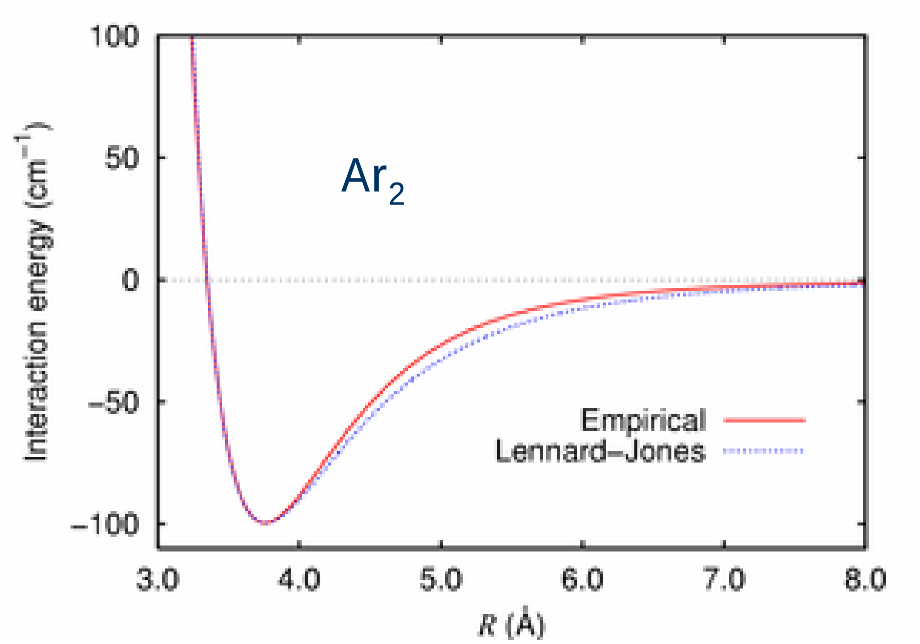
Entropy favors crystallization !

V. J. Anderson and H. N. W. Lekkerkerker, *Nature* **416** (2002) 811-815: Insights into phase transition kinetics from colloid science

Colloids

The Lennard-Jones potential (John Edward Lennard-Jones, 1894-1954):

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

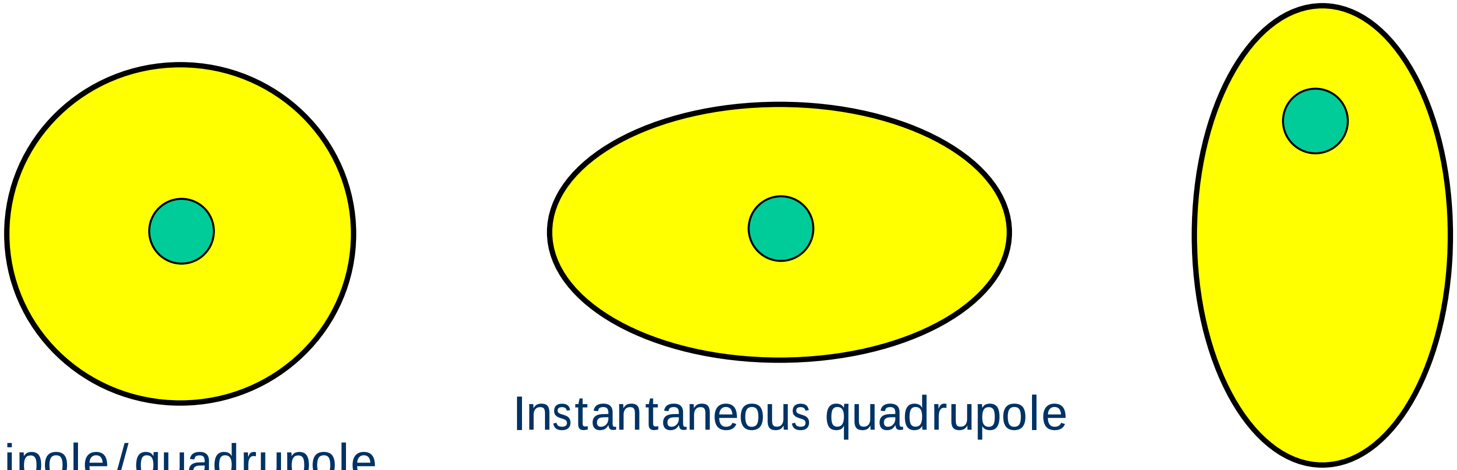


The attractive part is called the van der Waals attraction or (London) dispersion force. The repulsive part comes from the Pauli exclusion principle and the exponent is usually chosen for convenience.

wikipedia

Colloids

The dispersion force (van der Waals), London …. Arises from distortions in the electron cloud around nucleii:



No dipole/quadrupole

Instantaneous quadrupole

Instantaneous dipole

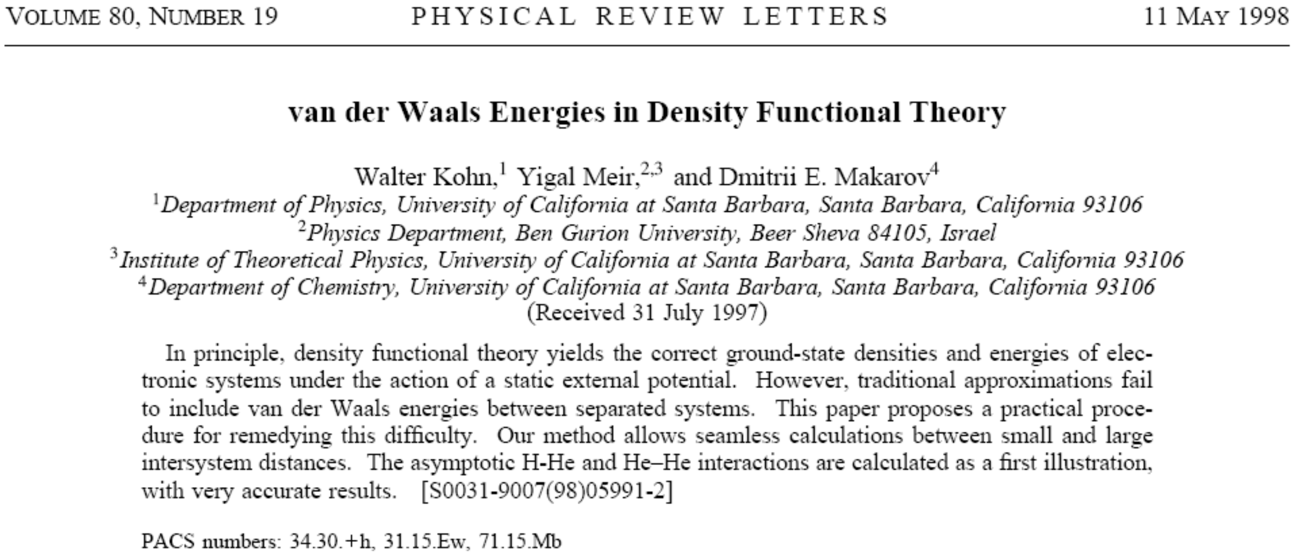
The London dispersion arises because of instantaneous dipoles forming in the floppy electron clouds of large atoms and molecules. It can trace its origins to the Heisenberg uncertainty principle.

The form is: $U(r) = -A/r^6$

Colloids

Why do we need potentials ?

1. Colloidal/soft matter systems are typically very large, with many points of contact (interaction). So despite the individual interactions being weak, the net effects are significant.
2. Computations on large systems (frequently) preclude complete quantum mechanical descriptions.
3. Standard applications of DFT, for example can fail to describe van der Waals type interactions.



VOLUME 80, NUMBER 19 PHYSICAL REVIEW LETTERS 11 MAY 1998

van der Waals Energies in Density Functional Theory

Walter Kohn,[1] Yigal Meir,[2,3] and Dmitrii E. Makarov[4]
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(Received 31 July 1997)

In principle, density functional theory yields the correct ground-state densities and energies of electronic systems under the action of a static external potential. However, traditional approximations fail to include van der Waals energies between separated systems. This paper proposes a practical procedure for remedying this difficulty. Our method allows seamless calculations between small and large intersystem distances. The asymptotic H-He and He–He interactions are calculated as a first illustration, with very accurate results. [S0031-9007(98)05991-2]

PACS numbers: 34.30.+h, 31.15.Ew, 71.15.Mb

Colloids

Colloidal particles are particles typically between 1 and a 1000 nm that can be dispersed (suspended) in fluids and for which Brownian forces are usually stronger than gravitation − the particles do not (usually) precipitate. Model colloidal particles are made of monodisperse spheres (polystyrene, silica …)

In suspension, the particles are attracted together by London dispersion. How does one keep them apart ?

In water, the colloidal particles can have like charges, for example, through attaching ionisable acid groups on the surface. These like charges repel, but the repulsion is usually screened. DLVO theory (Deryaguin-Landau-Verwey-Overbeek) puts together the attractive London part and the screened Coulomb repulsion:

Attraction: $U(r) = -A/r^6$

Repulsion: $U(r) \approx \frac{\exp(-\kappa r)}{r}$

Colloids

The screened Coulomb potential is given by Debye-Hückel theory, and arises because of all the charges due to ions in solution. κ^{-1} is the Debye screening length. When this is large, charges “see” one another easily, and when it is small, they do not.

Consequences for colloidal suspensions: In very clean (free from ions) solvents, the repulsions from the charges dominate.

In the presence of ions, the Coulombic repulsion is strongly *screened*, and the van der Waals attraction dominates.

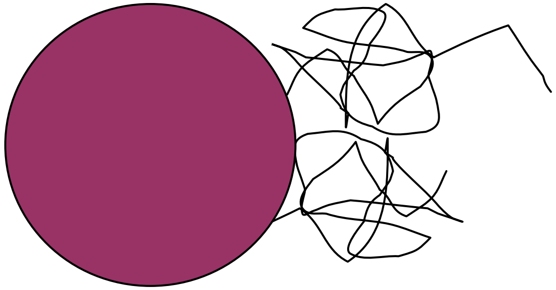
Thus for a suspension of colloidal spheres with ionisable surface groups, the phase behavior can be tuned.

Colloids

Polymers and steric stabilization:

Image colloidal particles in a non-polar solvent (an oil) of very low dielectric constant whence the particles would not ionize, and would not charge. How does one keep them apart ?

Answer: Stick polymeric chains on them. Entropic effects keep the chain bunched up. For another particle to approach, the chains on that particle must *interpenetrate* which implies the chains must straighten out. This is not entropically favored.



This is why gums are added to stabilize colloids (egg-whites in ice cream *etc.*)

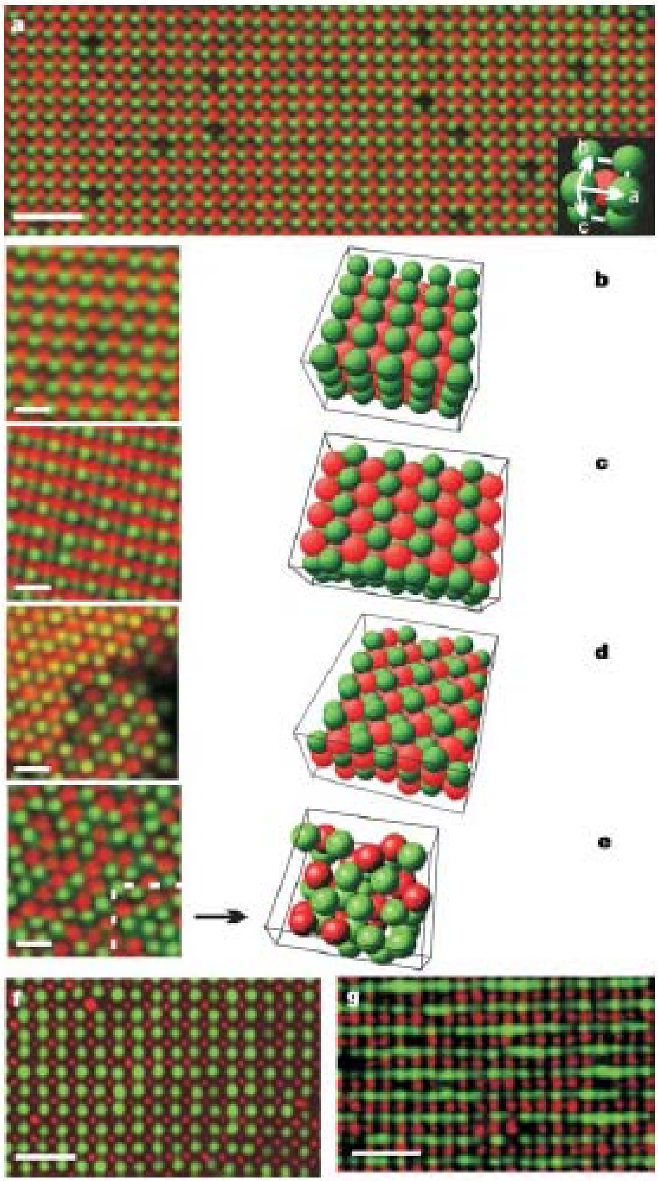
Colloids

Ionic colloidal crystals of oppositely charged particles

Mirjam E. Leunissen[1*], Christina G. Christova[1*], Antti-Pekka Hynninen[1], C. Patrick Royall[1]†, Andrew I. Campbell[1], Arnout Imhof[1], Marjolein Dijkstra[1], René van Roij[2] & Alfons van Blaaderen[1]

What can you do with colloids ? www.colloid.nl

Nature **437** (2005) 235



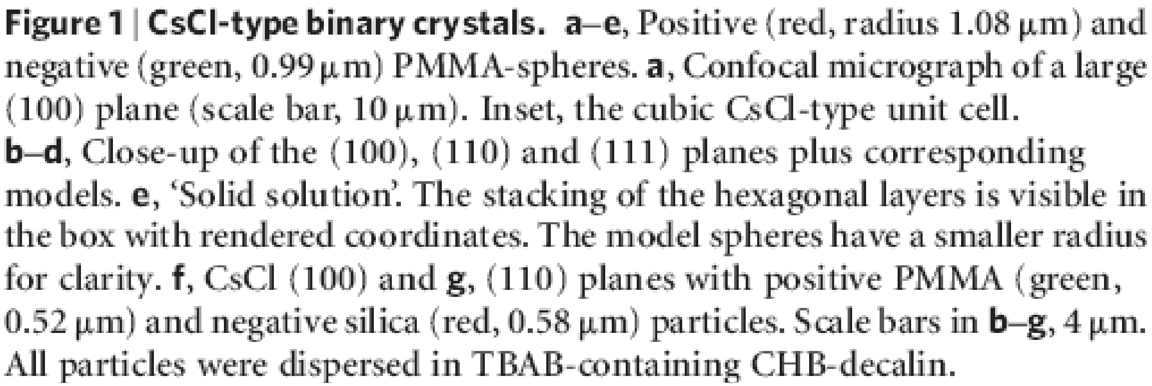


Figure 1 | CsCl-type binary crystals. a–e, Positive (red, radius 1.08 µm) and negative (green, 0.99 µm) PMMA-spheres. **a**, Confocal micrograph of a large (100) plane (scale bar, 10 µm). Inset, the cubic CsCl-type unit cell. **b–d**, Close-up of the (100), (110) and (111) planes plus corresponding models. **e**, 'Solid solution'. The stacking of the hexagonal layers is visible in the box with rendered coordinates. The model spheres have a smaller radius for clarity. **f**, CsCl (100) and **g**, (110) planes with positive PMMA (green, 0.52 µm) and negative silica (red, 0.58 µm) particles. Scale bars in **b–g**, 4 µm. All particles were dispersed in TBAB-containing CHB-decalin.

Colloids

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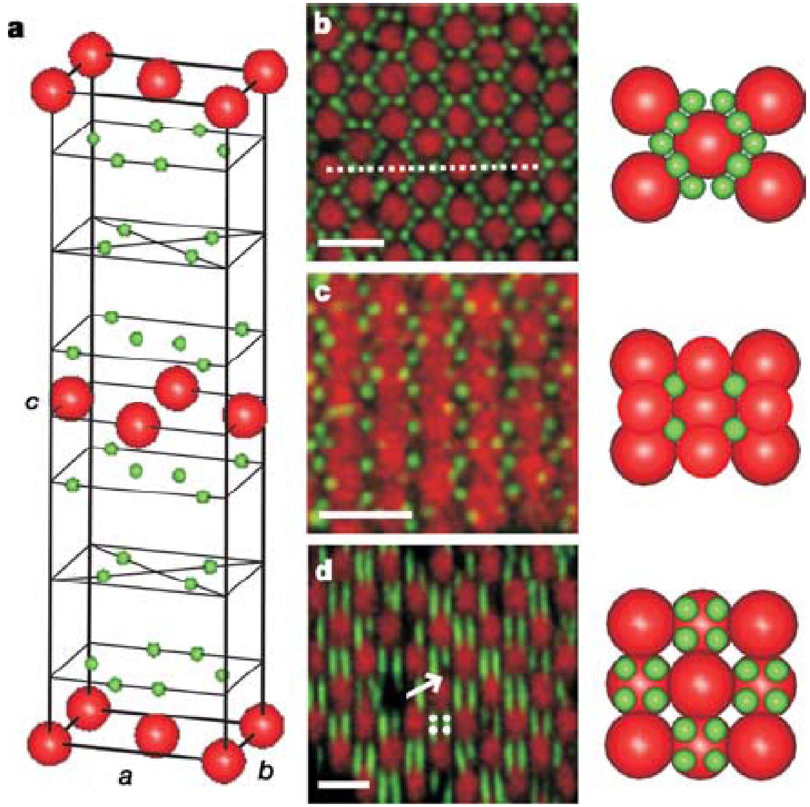

Figure 3 | LS_6-type binary crystals. a–d, Positive (green, radius 0.36 μm) and negative (red, 1.16 μm) PMMA-particles in TBAB-containing CHB-decalin, forming a structure with LS_6 stoichiometry. **a**, Unit cell with observed lattice spacings $a = 4.00$, $b = 2.84$ and $c = 4.7$ μm (not to scale for clarity). **b**, **c**, Confocal images and models of different *ab*-projections, showing a layer of large and several layers of small particles (**b**) and a plane with only small particles (**c**). **d**, *ac*-cut along the line in **b**. As the microscope could not completely resolve the four small particles in each octahedral hole, we indicated their positions with dots. The arrow indicates a missing particle. All scale bars are 4 μm.

What can you do with colloids ?
www.colloid.nl

Colloids

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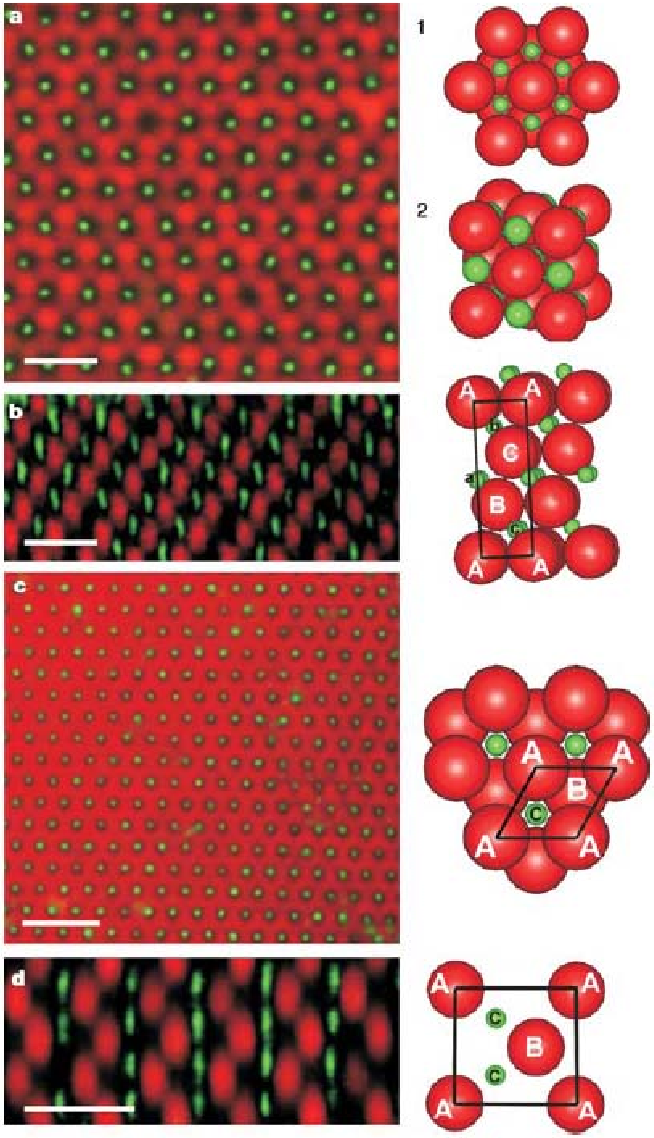


Figure 4 | LS-type binary crystals. Charged (red, radius 1.16 μm) and uncharged (green, 0.36 μm) PMMA-particles in CHB-decalin. **a**, **b**, NaCl-type crystal. **a**, Confocal image of the hexagonal plane and the unit cell in an hexagonal (1) and a cubic (2) representation (small spheres enlarged for clarity). **b**, Plane perpendicular to the hexagonal close packed layers, showing the *ABC*-stacking of both the large and small particles. **c**, **d**, NiAs-type crystal. **c**, Superposition of confocal images of ten layers and the corresponding model. **d**, Plane as in **b**, the model shows the *ABA*-stacking of the large and the *ccc*-stacking of the small particles (spheres not to scale). All scale bars are 8 μm.

Colloids

LETTERS

Self-assembly route for photonic crystals with a bandgap in the visible region

ANTTI-PEKKA HYNNINEN[1,2]*, JOB H. J. THIJSSEN[2], ESTHER C. M. VERMOLEN[2], MARJOLEIN DIJKSTRA[2] AND ALFONS VAN BLAADEREN[2]*

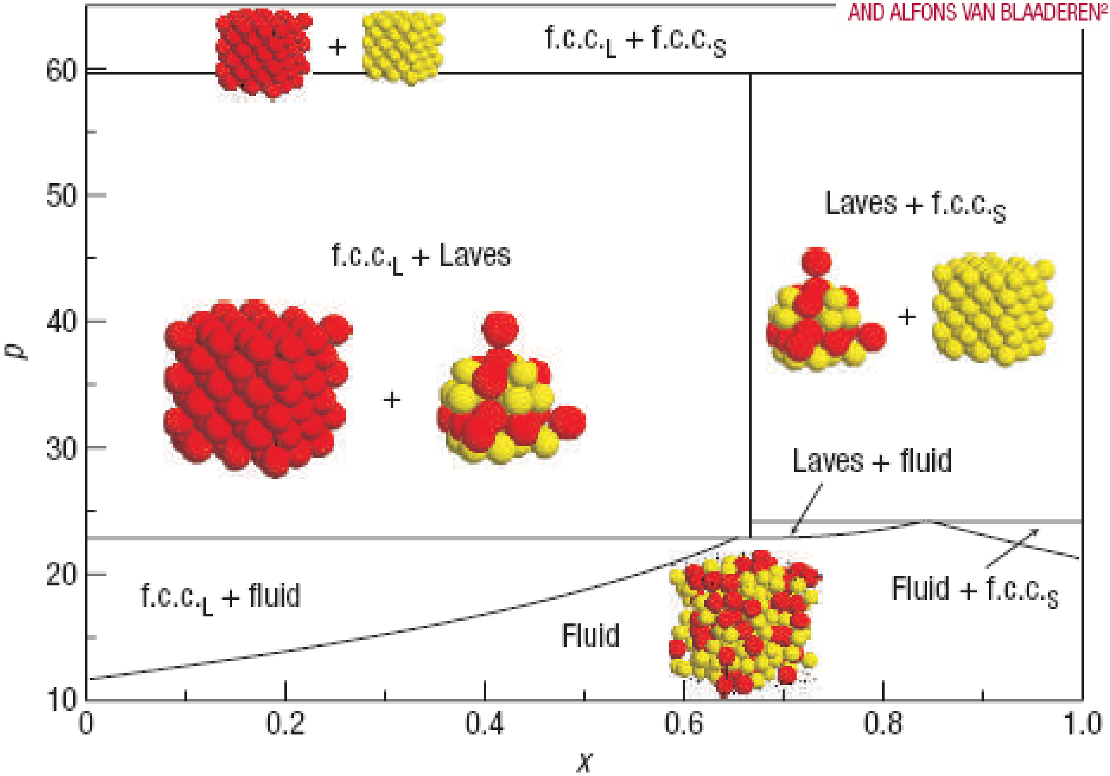
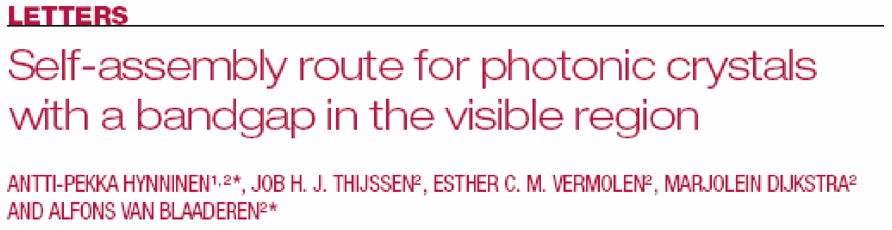


Figure 2 Phase diagram of binary hard spheres with a small-to-large size ratio of 0.82. The phase diagram is shown in the composition x, reduced pressure p, representation, where $x = N_S/(N_S + N_L)$ is the number fraction of small spheres. The labels 'f.c.c.$_L$' and 'f.c.c.$_S$' denote the f.c.c. crystals of large and small particles, respectively. The phase coexistence regions are labelled 'f.c.c.$_L$ + Laves', 'Laves + f.c.c.$_S$' and so on.

Nature Mater. **6** (2007) 202.

Colloids



LETTERS

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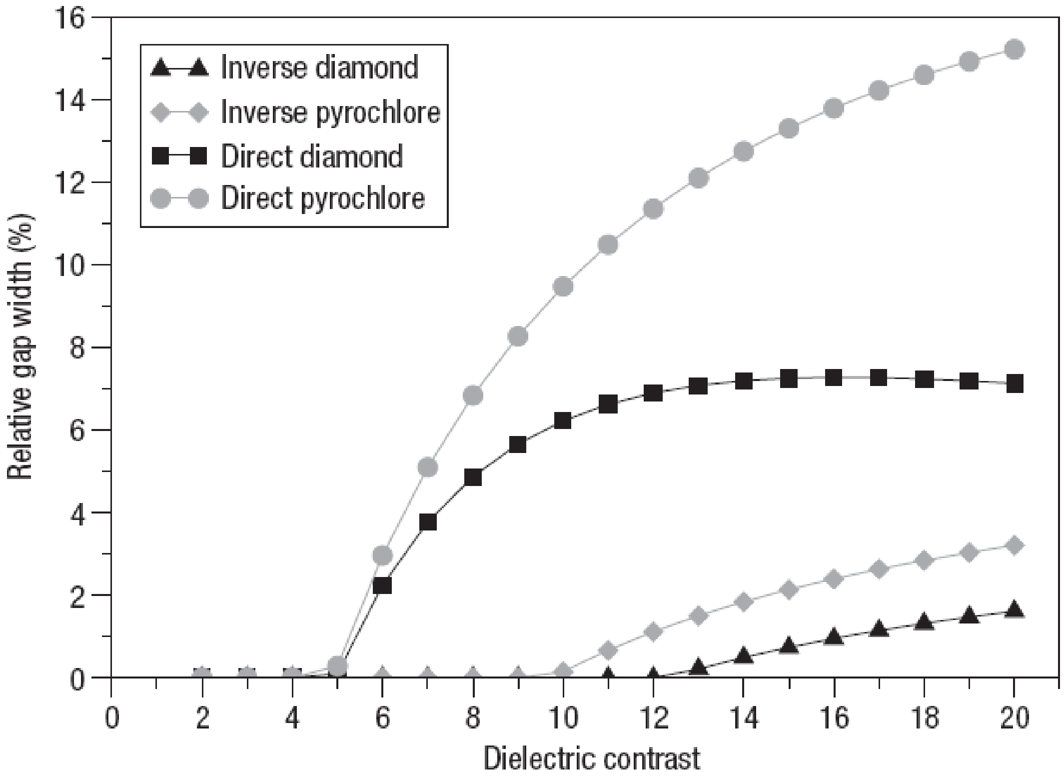

Nature Mater. **6** (2007) 202.

The atoms in the Laves phase can be described as interpenetrating diamond or pyrochlore lattices. Removing one leaves behind the other.